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LIGAND FIELD THEORY OF SUSCEPTIBILITY AND ANISOTROPY IN TRIGONALLY DISTORTED Fe^{2+} COMPLEXES

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(*Received February 3, 1965*)

ABSTRACT. Expressions for susceptibility and anisotropy of trigonally distorted Fe^{2+} complexes are deduced on the basis of the molecular orbital theory of Van Vleck (1935), Stevens (1953) and others (Bose *et al.*, 1960) and compared with the experimental results obtained by Mazumder *et al.*, (unpublished) and Jackson (1959) on $FeSiF_6$, $6H_2O$ consistently with structural and spectroscopic data. It is found that the spin-orbit coupling coefficients have to be decreased anisotropically from its free ion value indicating an anisotropic overlap between the central 3*d* and ligand *s*- and *p*-charge clouds. The increase in trigonal field coefficient Δ with temperature from a value of -1030 cm^{-1} at 7.85°K to -350 cm^{-1} at 300°K in $FeSiF_6$, $6H_2O$ is probably due to the thermal expansion and relaxation effects of the crystal lattice.

INTRODUCTION

In Fe^{2+} Tutton salts the assumption of a smal ltetragonal ligand field, comparable in magnitude to the spin-orbit coupling, superposed upon the predominant cubic field acting upon these ions, is found to give reasonable agreement with magnetic susceptibilities and anisotropies (Bose *et al*, 1961b). Pallumbo (1958) has tried to fit Jackson's (1959) susceptibility measurements of $FeSiF_6$, $6H_2O$ in the range 2°K to 77°K assuming a trigonal distortion of the field and with a formula based on the spin Hamiltonian approximation. This is not very satisfactory and also cannot explain quantitatively the detailed mean susceptibility and anisotropy measured recently in this laboratory. So we have deduced in the present paper expression for magnetic susceptibility and anisotropy of trigonally distorted [Fe^{2+}, $6H_2O$] complex on the basis of molecular orbital theory of Stevens (1953) and Bose *et al* (1960). The susceptibility measurements of Mazumder *et al* (unpublished) and Jackson (1959) (accurate to better than 0.5%) have been used to evaluate the theoretical parameters. It may be mentioned here that this salt belongs to the trigonal class (Pauling, 1930) with a single trigonally distorted [Fe^{2+}, $6H_2O$] octahedral complex in the unit cell, so that the principal ionic susceptibilities of this complex K_i ($i = \parallel$ or $\perp$ to the trigonal axis of the complex) can be directly obtained from the measured principal susceptibility values of the crystal.

MOLECULAR ORBITAL THEORY OF TRIGONALLY DISTORTED (Fe^{2+},$6H_2O$) COMPLEX

Under an octahedral field of the type O_h, $3d^6$ ^5D ground state of the free ion Fe^{2+} splits up to the extent 10580 cm^{-1} (Agnetta *et al* 1962) into a triplet $^5T_2$ and a doublet ^5E arising out of the configurations (considering a system consisting of four d holes) $(e_g)^2$ $(t_{2g})^2$ and $(e_g)^1$ $(t_{2g})^3$ respectively. The triplet state $^5T_2$ lies lowest, whose determinantal wavefunctions are (considering only the orbital part);

$$\begin{aligned}\psi_1 &= |e_a\ e_b\ t_b\ t_a| \\ \psi_2 &= |e_a\ e_b\ t_c\ t_a| \\ \psi_3 &= |e_a\ e_b\ t_a\ t_b|\end{aligned} \qquad \ldots (1)$$

which are inclusive of the overlap of the surrounding ligand s- and p- orbitals with central d-orbitals as given by :

$$\begin{aligned}t_a &= N\left[\ d_{xy} + \frac{\lambda}{2}(\pi_{x1}+\pi_{y2}+\pi_{x5}+\pi_{y4})\right] \\ t_b &= N\left[\ d_{yz} + \frac{\lambda}{2}(\pi_{x2}+\pi_{y3}+\pi_{x6}+\pi_{y5})\right] \\ t_c &= N\left[\ d_{xz} + \frac{\lambda}{2}(\pi_{x3}+\pi_{y1}+\pi_{x4}+\pi_{y6})\right] \\ e_a &= N'\left[\ d_{x^2-y^2} + \frac{\lambda'}{2}(\sigma_1+\sigma_4-\sigma_2-\sigma_5)\right] \\ e_b &= N'\left[\ d_{3z^2-r^2} + \frac{\lambda'}{2\sqrt{3}}(2\sigma_3+2\sigma_6-\sigma_1-\sigma_4-\sigma_2-\sigma_5)\right]\end{aligned} \qquad \ldots (2)$$

where N's are normalizing constants, λ's are the measure of the amounts of admixtures of the ligand s- and p-orbitals with the central d-orbitals. Here all σ-bonds are described by using z-coordinates; and π-bonds by using x and y-coordinates; all z-axes of the ligands pointing towards the metal atom.

The appropriate eigan states for the lowest triplet on quantization along the trigonal axis are

$$\begin{aligned}|+\rangle &= -\frac{1}{\sqrt{3}}[w|\psi_2\rangle + w^2|\psi_3\rangle + |\psi_1\rangle] \\ |0\rangle &= \frac{1}{\sqrt{3}}[|\psi_2\rangle + |\psi_3\rangle + |\psi_1\rangle] \\ |-\rangle &= \frac{1}{\sqrt{3}}[w^2|\psi_2\rangle + w|\psi_3\rangle + |\psi_1\rangle]\end{aligned} \qquad \ldots (3)$$

where $w = \exp\left(\frac{2\pi i}{3}\right)$ and ψ_1 etc., are given by (1). The overlap of the surrounding ligand s-and p-orbitals with the central d-orbitals introduces two orbital reduction factors defined by Griffiths (1961)

$$\left\langle t_{2\mu} \mid l_\lambda \mid t_{2\mu'} \right\rangle = \kappa \left\langle t'_{2\mu} \mid l_\lambda \mid t'_{2\mu'} \right\rangle$$

$$\left\langle t_{2\mu} \mid l_\lambda \mid e_{\mu'} \right\rangle = \kappa' \left\rangle t'_{2\mu} \mid l_\lambda \mid e'_{\mu'} \right\rangle \qquad \ldots \quad (4)$$

$$\left\langle e_\mu \mid l_\lambda \mid e_{\mu'} \right\rangle = 0$$

where $t'_{2\mu}$ and e'_μ are the original d-orbitals and $t_{2\mu}$ and e_μ are those admixed with the surrounding ligand orbitals. κ and κ' are orbital reduction factors generally unequal. On actual calculations of matrix element $\left\langle \psi_m \mid \vec{L} \mid \psi_n \right\rangle$ it is seen that so long as we are confined only to $^5T_2$ state of Fe^{2+}, only the factor κ is of importance since κ' does not occur, and the anisotropic reduction in ζ_i ($i = \parallel$ or $\perp$ to the trigonal axis of the ion) the spin-orbit coupling parameter from its free ion value is mainly due to the overlap of π-orbitals with the central d-orbitals.

FINE STRUCTURE

It can be shown that the set $\mid + \rangle$, $\mid 0 \rangle$ and $\mid - \rangle$ behaves as atomic P-state having $l'_\zeta = 1, 0, -1$ respectively and so the appropriate Hamiltonian for the lowest triplet state of the ion is (Abragam and Pryce 1951)

$$H = V_{trig} - \alpha\zeta_{\parallel} L_\zeta S_\zeta - \alpha'\zeta_\perp (L_\xi S_\xi + L_\eta S_\eta) \qquad \ldots \quad (5)$$

where L_ζ is along the trigonal axis of the crystal and L_ξ, L_η, L_ζ form a mutually orthogonal right handed set. α and α' are the effective orbital Lande' factors (Abragam and Pryce, 1951; Bose *et al*, 1961a) parallel or perpendicular to the trigonal axis, respectively, and includes the effect of the excited state ^5E upon the lowest $^5T_2$; ζ_i ($i = \parallel$ or $\perp$ to the trigonal axis) is the spin-orbit coupling coefficient reduced from its free ion value of -106 cm^{-1} due to covalency. Operating with the above Hamiltonian upon the atomic ^5P term and solving we get the eigen values and the new wavefunctions as follows :

$$\begin{aligned}
E_0 &= \tfrac{1}{2}[(\alpha\zeta_{\parallel} + \Delta) - \{(\alpha\zeta_{\parallel} - \Delta)^2 + 24\alpha'^2\zeta_\perp^2\}^{\frac{1}{2}}] \\
E_1 &= \alpha\zeta_{\parallel} x_1 \\
E_2 &= \tfrac{1}{2}[(\Delta - \alpha\zeta_{\parallel}) - \{(\Delta + \alpha\zeta_{\parallel})^2 + 8\alpha'^2\zeta_\perp^2\}^{\frac{1}{2}}] \\
E_3 &= \alpha\zeta_{\parallel} x_3 \qquad \ldots \quad (6) \\
E_4 &= \alpha\zeta_{\parallel}
\end{aligned}$$

$$E_5 = \tfrac{1}{2}[(\alpha\zeta_{||}+\Delta)+\{(\alpha\zeta_{||}-\Delta)^2+24\alpha'^2\zeta_\perp^2\}^{\frac{1}{2}}]$$
$$E_6 = \alpha\zeta_{||}x_6$$
$$E_7 = \tfrac{1}{2}[(\Delta-\alpha\zeta_{||})+\{(\Delta+\alpha\zeta_{||})+8\alpha'\zeta_\perp^2\}^{\frac{1}{2}}]$$
$$E_8 = -2\alpha\zeta_{||}$$

where x_j's are the roots of cubic eqn. :

$$x^3-x^2(2+\delta)+(2\delta-5\rho^2)x+6\rho^2 = 0$$

$$\rho = \frac{\alpha'\zeta_\perp}{\alpha\zeta_{||}} \; ; \; \delta = \frac{\Delta}{\alpha\zeta_{||}} \; , \qquad (7)$$

and Δ is the trigonal field separation between the split components (a doublet and a singlet) of the triplet $^5T_2$.

The corresponding eigenstates are :-

$$\phi_0 = a_0|1, -1\rangle + b_0|0, 0\rangle + a_0|-1, 1\rangle$$

$$\phi_1 = a_1|1, 0\rangle + b_1|0, 1\rangle + c_1|-1, 2\rangle$$

$$\phi_{1-} = a_1|-1, 0\rangle + b_1|0, -1\rangle + c_1|1, -2\rangle$$

$$\phi_2 = b_2|1, 1\rangle + a_2|0, 2\rangle$$

$$\phi_{2-} = b_2|-1, -1\rangle + a_2|0, -2\rangle$$

$$\phi_3 = a_3|1, 0\rangle + b_3|0, 1\rangle + c_3|-1, 2\rangle$$

$$\phi_{3-} = a_3|-1, 0\rangle + b_3|0, -1\rangle + c_3|1, -2\rangle \qquad \ldots (8)$$

$$\phi_4 = \frac{1}{\sqrt{2}}|1, -1\rangle - \frac{1}{\sqrt{2}}|-1, +1\rangle$$

$$\phi_5 = \frac{b_0}{\sqrt{2}}|1, -1\rangle - \sqrt{2}a_0|0, 0\rangle + \frac{b_0}{\sqrt{2}}|-1, +1\rangle$$

$$\phi_6 = a_6|1, 0\rangle + b_6|0, 1\rangle + c_6|-1, 2\rangle$$

$$\phi_{6-} = a_6|-1, 0\rangle + b_6|0, -1\rangle + c_6|1, -2\rangle$$

$$\phi_7 = a_2|1,\ 1\rangle - b_2|0,\ 2\rangle$$

$$\phi_{7-} = a_2|-1,\ -1\rangle - b_2|0,\ -2\rangle$$

$$\phi_8 = |1,\ 2\rangle$$

$$\phi_{8-} = |-1,\ -2\rangle$$

where

$$a_0 = \frac{\sqrt{3}\alpha'\zeta_\perp}{(\alpha\zeta_{||} - E_0)}\, b_0; \quad 2a_0^2 + b_0^2 = 1$$

$$a_j = -\frac{\sqrt{3}(2\alpha\zeta_{||} - E_j)}{\sqrt{2}E_j}\, c_j\ ; \quad a_j^2 + b_j^2 + c_j^2 = 1 \qquad \ldots (9)$$

$$b_j = \frac{2\alpha\zeta_{||} - E_j}{\sqrt{2}\zeta}\, c_j \qquad j = 1,\ 3,\ 6$$

and $$a_2 = \frac{\sqrt{2}\alpha'\zeta_\perp}{\Delta - E_2}\, b_2\ ; \quad a_2^2 + b_2^2 = 1$$

EXPRESSION FOR SUSCEPTIBILITY

As usual calculating the effect of the magnetic perturbations $\beta H(-\alpha L + 2S)$ upto the second order, we get the expressions for principal magnetic susceptibility $K_i (i = ||$ or $\perp$ to the trigonal axis of the crystal) as given below :

$$K_{||} = \frac{N\beta^2}{kW}\Big[\frac{1}{T}\Big\{\sum_{j=1,3,6} 2[\alpha\kappa_{||}(c_j^2 - a_j^2) + 2b_j^2 + 4c_j^2]^2 \exp\Big(-\frac{E_j - E_0}{kT}$$

$$+ 2[b_2^2(2 - \alpha\kappa_{||}) + 4a_2^2]^2 \exp\Big(-\frac{E_2 - E_0}{kT}\Big)$$

$$+ 2[a_7^2(2 - \alpha\kappa_{||}) + 4b_7^2]^2 \exp\Big(-\frac{E_7 - E_0}{kT}$$

$$+ 2[(4 - \alpha\kappa_{||})^2] \exp\Big(-\frac{E_8 - E_0}{kT}\Big)\Big\} \qquad \ldots (10)$$

$$+ 2k\Big\{\frac{2a_0^2(2 + \alpha\kappa_{||})^2}{E_4 - E_0} + G_{22}^{\ 1} \exp\Big(-\frac{E_1 - E_0}{kT}\Big)$$

$$+\frac{2a_1^2b_2^2(2+\alpha\kappa_{\|})^2}{E_7-E_2}\exp\left(-\frac{E_2-E_0}{kT}\right)+G_{2z}^3\exp\left(-\frac{E_3-E_0}{kT}\right)$$

$$+G_{2z}^0\exp\left(-\frac{E_4-E_0}{kT}\right)-\frac{b_0^2(2+\alpha\kappa_{\|})}{E_5-E_4}\exp\left(-\frac{E_5-E_0}{kT}\right)$$

$$+G_{2z}^6\exp\left(-\frac{E_6-E_0}{kT}\right)-\frac{2c_2^2b_2^2(2+\alpha\kappa_{\|})^2}{E_7-E_2}\exp\left(-\frac{E_7-E_0}{kT}\right)\Big\}\Big]$$

where

$$G_{2z}^1=R_{31}+R_{61};\ G_{2z}^3=-R_{31}+R_{63};\ G_{2z}^6=-R_{63}-R_{61}$$

$$R_{ij}=\frac{2[\alpha\kappa_{\|}(c_ic_j-a_ia_j)+2b_ib_j+4c_ic_j]^2}{E_i-E_j} \qquad \ldots\ (11)$$

$$G_{2z}^0=-\frac{2a_0^2(2+\alpha\kappa_{\|})^2}{E_4-E_0}+\frac{b_0^2(2+\alpha\kappa_{\|})^2}{E_5-E_4}$$

$$W=\Big[1+2\exp\left(-\frac{E_1-E_0}{kT}\right)+2\exp\left(-\frac{E_2-E_0}{kT}\right)+2\exp\left(-\frac{E_3-E_0}{kT}\right)$$

$$+\exp\left(-\frac{E_4-E_0}{kT}\right)+\exp\left(-\frac{E_5-E_0}{kT}\right)+2\exp\left(-\frac{E_6-E_0}{kT}\right)$$

$$+2\exp\left(-\frac{E_7-E_0}{kT}\right)+2\exp\left(-\frac{E_8-E_0}{kT}\right)\Big] \qquad \ldots\ (12)$$

and

$$K_{\perp}=\frac{2N\beta^2}{W}\Big[G_{2x}^0+G_{2x}^1\exp\left(-\frac{E_1-E_0}{kT}\right)+G_{2x}^2\exp\left(-\frac{E_2-E_0}{kT}\right)$$

$$+G_{2x}^3\exp\left(-\frac{E_3-E_0}{kT}\right)+G_{2x}^4\exp\left(-\frac{E_4-E_0}{kT}\right)$$

$$+G_{2x}^5\exp\left(-\frac{E_5-E_0}{kT}\right)+G_{2x}^6\exp\left(-\frac{E_6-E_0}{kT}\right)$$

$$+G_{2x}^7\exp\left(-\frac{E_7-E_0}{kT}\right)+G_{2x}^8\exp\left(-\frac{E_8-E_0}{kT}\right)\Big] \qquad \ldots\ (13)$$

$$\phi_7 = a_2|1,\ 1\rangle - b_2|0,\ 2\rangle$$

$$\phi_{7-} = a_2|-1,\ -1\rangle - b_2|0,\ -2\rangle$$

$$\phi_8 = |1,\ 2\rangle$$

$$\phi_{8-} = |-1,\ -2\rangle .$$

where

$$a_0 = \frac{\sqrt{3}\alpha'\zeta_\perp}{(\alpha\zeta_{\|} - E_0)}\, b_0; \quad 2a_0^2 + b_0^2 = 1$$

$$a_j = -\frac{\sqrt{3}(2\alpha\zeta_{\|} - E_j)}{\sqrt{2}E_j}\, c_j\ ; \quad a_j^2 + b_j^2 + c_j^2 = 1 \qquad \ldots\ (9)$$

$$b_j = \frac{2\alpha\zeta_{\|} - E_j}{\sqrt{2}\zeta}\, c_j \qquad j = 1, 3, 6$$

and $$a_2 = \frac{\sqrt{2}\alpha'\zeta_\perp}{\Delta - E_2}\ b_2\ ; \quad a_2^2 + b_2^2 = 1$$

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$$+ 2[b_2^2(2 - \alpha\kappa_{\|}) + 4a_2^2]^2 \exp\Big(-\frac{E_2 - E_0}{kT}\Big)$$

$$+ 2[a_2^2(2 - \alpha\kappa_{\|}) + 4b_2^2]^2 \exp\Big(-\frac{E_7 - E_0}{kT}\Big)$$

$$+ 2[(4 - \alpha\kappa_{\|})^2] \exp\Big(-\frac{E_8 - E_0}{kT}\Big)\Big\} \qquad \ldots\ (10)$$

$$+ 2k\Big\{\frac{2a_0^2(2 + \alpha\kappa_{\|})^2}{E_4 - E_0} + G_{zz}^1 \exp\Big(-\frac{E_1 - E_0}{kT}\Big)$$

$$+\frac{2a_2^2b_2^2(2+\alpha\kappa_{||})^2}{E_7-E_2}\exp\left(-\frac{E_2-E_0}{kT}\right)+G_{2z}^3\exp\left(-\frac{E_3-E_0}{kT}\right)$$

$$+G_{2z}^0\exp\left(-\frac{E_4-E_0}{kT}\right)-\frac{b_0^2(2+\alpha\kappa_{||})}{E_5-E_4}\exp\left(-\frac{E_5-E_0}{kT}\right)$$

$$+G_{2z}^6\exp\left(-\frac{E_6-E_0}{kT}\right)-\frac{2a_2^2b_2^2(2+\alpha\kappa_{||})^2}{E_7-E_2}\exp\left(-\frac{E_7-E_0}{kT}\right)\Big\}\Big]$$

where

$$G_{2z}^1=R_{31}+R_{61};\ G_{2z}^3=-R_{31}+R_{63};\ G_{2z}^6=-R_{63}-R_{61}$$

$$R_{ij}=\frac{2[\alpha\kappa_{||}(c_ic_j-a_ia_j)+2b_ib_j+4c_ic_j]^2}{E_i-E_j}$$

$$G_{2z}^0=-\frac{2a_0^2(2+\alpha\kappa_{||})^2}{E_4-E_0}+\frac{b_0^2(2+\alpha\kappa_{||})^2}{E_5-E_4} \qquad \text{... (11)}$$

$$W=\Big[1+2\exp\left(-\frac{E_1-E_0}{kT}\right)+2\exp\left(-\frac{E_2-E_0}{kT}\right)+2\exp\left(-\frac{E_3-E_0}{kT}\right)$$

$$+\exp\left(-\frac{E_4-E_0}{kT}\right)+\exp\left(-\frac{E_5-E_0}{kT}\right)+2\exp\left(-\frac{E_6-E_0}{kT}\right)$$

$$+2\exp\left(-\frac{E_7-E_0}{kT}\right)+2\exp\left(-\frac{E_8-E_0}{kT}\right)\Big] \qquad \text{... (12)}$$

and

$$K_\perp=\frac{2N\beta^2}{W}\Big[G_{2x}^0+G_{2x}^1\exp\left(-\frac{E_1-E_0}{kT}\right)+G_{2x}^2\exp\left(-\frac{E_2-E_0}{kT}\right)$$

$$+G_{2x}^3\exp\left(-\frac{E_3-E_0}{kT}\right)+G_{2x}^4\exp\left(-\frac{E_4-E_0}{kT}\right)$$

$$+G_{2x}^5\exp\left(-\frac{E_5-E_0}{kT}\right)+G_{2x}^6\exp\left(-\frac{E_6-E_0}{kT}\right)$$

$$+G_{2x}^7\exp\left(-\frac{E_7-E_0}{kT}\right)+G_{2x}^8\exp\left(-\frac{E_8-E_0}{kT}\right)\Big] \qquad \text{... (13)}$$

where

$$G_{2x}{}^0 = \frac{2A_{01}{}^2}{E_1-E_0} + \frac{2A_{03}{}^2}{E_3-E_0} + \frac{2A_{06}{}^2}{E_6-E_0}$$

$$G_{2x}{}^1 = -\frac{2A_{01}{}^2}{E_1-E_0} + \frac{2B_{21}{}^2}{E_2-E_1} + \frac{2A_{41}{}^2}{E_4-E_1} + \frac{2A_{51}{}^2}{E_5-E_1} + \frac{2B_{71}{}^2}{E_7-E_1}$$

$$G_{2x}{}^2 = -\frac{2B_{21}{}^2}{E_2-E_1} + \frac{2B_{23}{}^2}{E_3-E_2} + \frac{2B_{26}{}^2}{E_6-E_2} + \frac{2(2b_2-\alpha'\kappa_\perp a_2\sqrt{2}}{E_8-E_2}$$

$$G_{2x}{}^3 = -\frac{2A_{03}{}^2}{E_3-E_0} - \frac{2B_{23}{}^2}{E_3-E_2} + \frac{2A_{43}{}^2}{E_4-E_3} + \frac{2A_{53}{}^2}{E_5-E_3} + \frac{2B_{73}{}^2}{E_7-E_3}$$

$$G_{2x}{}^4 = -\frac{2A_{41}{}^2}{E_4-E_1} - \frac{2A_{43}{}^2}{E_4-E_3} + \frac{2A_{46}{}^2}{E_6-E_4}$$

$$G_{2x}{}^5 = -\frac{2A_{51}{}^2}{E_5-E_1} - \frac{2A_{53}{}^2}{E_5-E_3} + \frac{2A_{56}{}^2}{E_6-E_5}$$

$$G_{2x}{}^6 = -\frac{2A_{06}{}^2}{E_6-E_0} - \frac{2B_{26}{}^2}{E_6-E_2} - \frac{2A_{46}{}^2}{E_6-E_4} - \frac{2A_{56}{}^2}{E_6-E_5} + \frac{2B_{76}{}^2}{E_7-E_6} \qquad (14)$$

$$G_{2x}{}^7 = -\frac{2B_{71}{}^2}{E_7-E_1} \quad \frac{2B_{73}{}^2}{E_7-E_3} \quad \frac{2B_{76}{}^2}{E_7-E_6} \quad \frac{2\left(2a_2-\frac{\alpha'\kappa_\perp b_2}{\sqrt{2}}\right)^2}{E_8-E_7}$$

$$G_{2x}{}^8 = -\frac{2\left(2a_2-\frac{\alpha'\kappa_\perp b_2}{\sqrt{2}}\right)^2}{E_8-E_7} \quad \frac{2\left(2b_2-\frac{\alpha'\kappa_\perp a_2}{\sqrt{2}}\right)^2}{E_8-E_7}$$

where

$$A_{0j} = \sqrt{6}(a_0a_j+b_0b_j) - \frac{\alpha'\kappa_\perp}{\sqrt{2}}(a_jb_0+b_ja_0)+2c_ja_0$$

$$B_{2j} = (\sqrt{6}b_2a_j+2a_2b_j) - \frac{\alpha\kappa_\perp}{\sqrt{2}}(b_2b_j+a_2c_j)$$

$$A_{4j} = \sqrt{3}a_j + \frac{b_j\kappa_\perp}{2} - \sqrt{2}c_j \qquad (15)$$

$$A_{5j} = \sqrt{3}(b_0a_j - 2a_0b_j) - \frac{\alpha'\kappa_\perp}{2}(b_0b_j - 2a_0a_j) + \sqrt{2}b_0b_j$$

$$B_{7j} = (\sqrt{6}a_2a_j - 2b_2b_j) - \frac{\alpha'\kappa_\perp}{2}(b_ja_2 - c_jb_2)$$

g-VALUES

If we take Δ to be positive, on including the spin-orbit coupling a doublet (ϕ_1, ϕ_{1-}) comes to occupy the lowest position giving $g_\parallel \approx 8$ and $g_\perp \approx 0$ (Bose *et al*, 1961b) which requires $K_\parallel$ to be greater than $K_\perp$. Recent neutron diffraction studies of the salt (Hamilton, 1962) seem to indicate that the trigonal axis of $[Fe^{2+}, 6H_2O]$ cluster in this salt is elongated and we would expect a priori that $g_\parallel > g_\perp$ as roughly calculated above. On the contrary, the magnetic measurement definitely shows that the trigonal axis of the crystal sets normally to the magnetic field and hence $\chi_\perp > \chi_\parallel$ or $K_\perp > K_\parallel$ (since the unit cell contains one ion only). This shows that the criterion for $g_\parallel >$ or $< g_\perp$ depends on other factors as well in addition to ligand distances e.g. the charge densities, overlap etc. Also, it is evident that Δ must be negative.

For a negative value of Δ the wavefunctions, as arranged in (9), are in the order of increasing energies and the singlet ϕ_0 lies lowest with doublet (ϕ_1, ϕ_{1-}) close to it. The system behaves for most purposes as with effective spin 1. g-value expressions are

then

$$g_\parallel = [\alpha\kappa_\parallel(c_1^2 - a_1^2) + 2b_1^2 + 4c_1^2] \qquad \ldots (16)$$

$$g_\perp = \sqrt{2}\left[\sqrt{6}(a_0a_1 + b_0b_1) - \frac{\alpha'\kappa_\perp}{\sqrt{2}}(a_1b_0 + b_1a_0) + 2c_1a_0\right]$$

No experimental resonance data for $g_\parallel$, $g_\perp$ on $FeSiF_6$, $6H_2O$ are available. However the mean g-value = 3.30 calculated indirectly from susceptibility is close to Low's result ($\bar{g} = 3.41$; Low, 1960) on hexacoordinated Fe^{2+} ion embedded in MgO. Crystal field in this latter salt is perfectly cubic, which along with spin-orbit coupling alone is not sufficient to remove the degeneracy of the ground level ; three-fold degeneracy remains in the ground state, which is responsible for Jahn-Teller instability. An isotropic g-value is obtained (Low, 1960, Opik and Pryce, 1951). In $FeSiF_6 6H_2O$ however, this degeneracy is partly lifted by the introduction of the trigonal field; the g-value becomes anisotropic. It appears that the introduction of the trigonal asymmetry in the ligand cluster does not make much difference in the mean g-value from the above cubic case. These values may be compared with the mean g-values for $\Delta = +ve$, in

$Fe(NH_4SO_4)_2$, $6H_2O$ ($\bar{g} = 3.0$ Bose *et al* 1961*b*) and FeF_2 embedded in ZnF_2($\bar{g} = 2.99$; Tinkham, 1955) in which the Fe^{2+} ions have approximately tetragonal and orthorhombic symmetry, respectively.

DISCUSSIONS ON EXPERIMENTAL MEAN SUSCEPTIBILITIES AND ANISOTROPY

Symmetry considerations of the ligand clusters discussed above apply in general equally to the magnetic susceptibility and anisotropy. The theoretical parameters Δ, $\alpha\zeta_{||}$, $\alpha'\zeta_{\perp}$ and $\alpha\kappa_{||}$, $\alpha' k_{\perp}$ fitting the experimental magnetic mean susceptibility and anisotropy have been uniquely calculated within an error of about 0.5% by extensive trial and error method described elsewhere (Bose *et al*, 1964) consistent with spectroscopic absorption data.

The coefficients α, α', $\zeta_{||}$, ζ and $\kappa_{||}$, $\kappa_{\perp}$ can not be calculated separately since they appear as products, in the equations mentioned above, though reasonable estimates may be made of the anisotropic reductions in the ideal values of the coefficients, namely $\zeta_{||} = \zeta_{\perp} = -106\ cm^{-1}$ for the free ion, $\alpha = \alpha' = 1$ in a cubic field and $\kappa_{||} = \kappa_{\perp} = 1$ for no overlap.

The level (ϕ_1, ϕ_{1-}) just above the ground level ϕ_0 starts getting depopulated quickly in the liquid hydrogen temperature range (energy separation being $\sim$ 10 cm^{-1}), causing a comparatively rapid fall in experimental effective moment square $\bar{p}^2$ versus T curve, as also a hump in the ($p_{\perp}^2 - p_{||}^2$) versus T curve in this region. No thermal phase transition has been observed in this salt as in the isomorphous Co^{2+} (Bose *et al*, 1965) and Cu^{2+} fluosilicates (Mazumder *et al*, unpublished). The experimental data for both mean susceptibility and anisotropy fit nicely with a unique set of theoretical parameters (given in Table I) at each temperature in the entire range 300°K–7.85°K, only when Δ is made to vary with temperature and a temperature dependent field separation Δ with a continuous increase from $-1025\ cm^{-1}$ at 7.85°K to $-350\ cm^{-1}$ at 300°K is taken. The variation in Δ is apparently somewhat exaggerated since we assumed the anisotropies in the other parameters though related to Δ, as independent of temperature for the sake of keeping the uniqueness of the trial and error calculations. The cubic and the Coulomb fields may of course be reasonably taken to be independent. The said exaggerated variation in Δ might be reduced reasonably if we had independent thermal variation data of spectroscopic absorption or para-magnetic resonance. But in the absence of these we are not able to make further refinement for the present.

One apparently anomalous situation needs a further remark or two. As seen in the case of $FeSiF_6$, $6H_2O$ the relative elongation or contraction of the axial principal directions as observed by neutron-diffraction does not seem to have any direct bearing on the relative magnitudes of the susceptibility tensors, as frequently assumed by many workers. A further example is provided by the recent accurate X-ray investigation (Grimes *et al* 1963) on $Ni(NH_4SO)_2$, $6H_2O$, indicating a strict

tetragonal symmetry of [Ni^{2+}, $6H_2O$] clusters, whereas both the paramagnetic resonance and magnetic anisotropy measurements indicate a rather large orthorhombic symmetry. Moreover, the tetragonal axis found by X-ray is quite different from the approximate tetragonal axis found from anisotropy and resonance calculations, and again the X-ray data gives the tetragonal axis as elongated, whereas the approximately tetragonal magnetic tensor axis is characterised by

$$K_\perp (= K_1 \approx K_2) > K_\parallel (= K_3)$$

This is not surprising if we note that the anisotropic ligand field effect upon the central ion is not a function of distance alone but is quite sensitively dependent upon small ligand charge orientations and overlaps.

TABLE I

$FeSiF_6.6H_2O$. Temperature variation of mean moment sq ($\bar{p}^2$ and) anisotropy ($p_\perp{}^2 - p_\parallel{}^2$)

Temp. °K	Δcm^{-1}	$p_\perp{}^2 - p_\parallel{}^2$	p^2	Mean g-value
300	-350	6.76	27.64	
		(6.73)	(27.66)	
180	−750	8.84	27.55	
		(8.80)	(27.53)	
140	−925	9.90	27.40	
		(9.92)	(27.40)	
20.4	−1000	25.68	24.55	3.30
		(25.64)	(24.46)	(3.34)
14.2	−1025	26.71	22.97	
		(26.62)	(22.99)	
7.85	−1030	26.00	19.86	
		(26.06)	(19.88)	

The values within parantheses are from experiments of L. C. Jackson (1959) and Mazumdor *et al.*, unpublished.

$$\alpha\zeta_\parallel = P_\parallel = -104 \text{ cm}^{-1} \qquad \alpha\kappa_\parallel = Q_\parallel = 0.50$$

$$\alpha'\zeta_\perp = P_\perp = -98 \text{ cm}^{-1} \qquad \alpha'\kappa_\perp = Q_\perp = 0.70$$

APPENDIX

Expression for α and α' in the case of Fe^{2+}

Wavefunctions of the lowest triplet state of Fe^{2+} under trigonal field, which admixes the excited doublet E_g with the split doublet component of T_{2g}, say $T_{2g}\pm$ is in $|LM_L>$ scheme are,

$$\psi_+ = \epsilon\left[\sqrt{\frac{2}{3}}\,|22>-\sqrt{\frac{1}{3}}\,|2-1>\right]+\tau\left[\sqrt{\frac{1}{3}}\,|22>+\sqrt{\frac{2}{3}}\,|2-1>\right]$$

$$\psi_- = \epsilon\left[\sqrt{\frac{2}{3}}\,|2-2>+\sqrt{\frac{1}{3}}\,|21>\right]+\tau\left[\sqrt{\frac{1}{3}}\,|2-2>-\sqrt{\frac{2}{3}}\,|21>\right] \quad (17)$$

$$\psi_0 = |20>$$

So that a calculation similar to Pryce for Co^{2+} (1951) yields

$$\alpha = \epsilon^2+2\sqrt{2}\epsilon\tau$$

$$\alpha' = \epsilon-\sqrt{2}\tau \quad \ldots \quad (18)$$

$$\epsilon^2+\tau^2 = 1$$

Expression (18) is applicable in all the cases where the lowest state is D-state and the asymmetric field is a trigonal one.

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